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The absence of a single viewpoint on the nature of the oxidative-reduction potentials of polymer redoxites [1,2] leads to the necessity of a more detailed examination of their behavior.

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The soluble redoxites. Their activity does not noticeably change, as a result of the fact that the functional groups are in the polymer molecule and do not emerge in the free state. In the simplest case, the value of the oxidative-reduction potential depends on the degree of oxidation F of the redoxite:

$$\varphi = \varphi^0 + \frac{RT}{zF} \ln \frac{F}{1-F}, \quad (1)$$

where φ^0 is the potential by half the oxidized resin. Here it is assumed that electron migration occurs as the result of electrical conductivity of the linear chain between the separate regions of the macromolecule. If the electron transfer is difficult, a quite large interval of time is required for the onset of equilibrium. The process is even more complicated when the bonding radical is not electrically conducting and reaction of the separate groups proceeds through the spatial effect of each on the other, within the limits of one or more macromolecules. The structural

* Numbers in margin indicate pagination in original foreign text.

characteristics determine the practical deviations from general theoretical principles that are frequently observed [1,3].

Insoluble redoxites. In cross-linked electron exchangers, the equilibrium between the oxidized and reduced particles basically occurs locally. If the electron migration between all groups of the matrix is possible, then dynamic equilibrium ensues over the course of a quite long period of time. This is apparently more characteristic of the redoxites with a system of linkage and with semiconductor properties [4]. With respect to the solid redoxites with electrical conductivity and infinitely small migration flux, the concept of the oxidative-reduction potential cannot correspond to any actual potential-determining process [5].

The problem of the relationship of the equilibrium potential and the degree of redox-conversion is solved in most cases proceeding from the fact that a polymer with firmly cross-linked oxidative and reduction groups is in the form of a solid solution [1]. The degree of conversion during this process depends on the activities of the oxidized and reduced forms, just as it does for soluble polymers or monomers, being subordinate to Equation (1). However, inasmuch as the reaction between the solid redoxite and the solution is heterogeneous, another hypothesis relating to the fact that the activities of both forms are constant and equal to unity is more probable [6]. Then the state of equilibrium is determined only by the relationship of activities of the dissolved reaction components with any proportions of amounts of the oxidized and reduced forms of the resin, and the degree of conversion F will not be a function of the oxidative-reduction potential of the solution. / 614

Experiments were set up to investigate the nature of the redox processes and the potentials of solid granular EO-7 redoxiates with quinone-hydroquinone groups in the phenol-formaldehyde matrix, and EI-5 redoxite with finely dispersed metallic copper

in the pores of the KU-11 sulfocationite responsible for them, in order to make an experimental check of this hypotheses [7].

Measurement of the potentials was carried out by the aid of a mercury electrode on whose surface a resin layer 3-5 mm in thickness was placed. The accuracy of the measurements was 10^{-4} v. The investigation of the reaction equilibrium of the redoxite with the dissolved oxidative-reduction pair $\text{Fe}^{3+}/\text{Fe}^{2+}$ was carried out in an unaerated, continuously mixed solution. Control over the course of the reaction was carried out by means of colorimetric analysis of the solution, with simultaneous measurement of the potentials of the indicator platinum electrodes. The error of the experiment was $\sim 7-9\%$.

If the quinone-hydroquinone resin has the capacity to link the oxidative-reduction potential to the inert electrode, its thermodynamic value should correspond to the Equation (1). As can be seen from Figure 1,a, the experimental points corresponding to the steady potentials of the mercury electrode dressed with EO-7 redoxite oxidized to various degrees, have a nearly straight line in coordinates $\varphi - \ln(F/1-F)$, the tangent of whose angle of inclination is 0.003v, as opposed to a theoretical value of 0.029v. Figure 1,b, indicates the determinative role of the degree of granulation of the polymer: large granules do not practically alter the potential of the mercury electrode, while at the same time small resin particles lead to a change in potential on the positive side. But all the same, the standard potential, changing somewhat depending on the degree of oxidation and granulation, does not reflect the equilibrium state of the quinone-hydroquinone pair consisting of grains of the EO-7 polymer electron exchange material.

The indirect method of estimating the oxidative-reduction potential consisted in investigating the equilibrium conversion of the resin in contact with the inverse redox-pair $\text{Fe}^{3+}/\text{Fe}^{2+}$.

The equilibrium constant of the oxidation process of the EO-7 polymer by iron ions at $\text{pH}=0$ and accomplishment of Equation (1) are expressed in the form

$$c = \frac{\bar{a}_x \cdot c_{\text{Fe}^{3+}}^2}{\bar{a}_{\text{Fe}^{2+}} \cdot a_{\text{H}^+}^2}, \quad (2)$$

while with a constant and even unit of activity of the solid phases, the second member of Equation (1) reverts to 0 and

$$c = \left(\frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \right)^2. \quad (3)$$

Using f to indicate the degree of conversion of the dissolved component and the α -ratio of the initial quantities of the oxidative-reduction groups in the solution and the redoxite, we present Equation (2) in the form

$$(1-c^{-1})\alpha f^2 - (2\alpha+1)f + (2+\alpha)f-1=0. \quad (4)$$

Correspondingly, from (3) we find

$$f(c^{1/2}+1)-1=0. \quad (5) \quad \underline{615}$$

Based on expression (4), (5) and the experimentally established relationship of f and α , one can draw a conclusion on the nature of the redox process. The table shows the calculated values of the degree of conversion of ions of bivalent iron drawn into reaction with the quinone form of redoxite.

From the table one can see that the experimental value of f preserves its constancy in the course of the change in the redoxite dressing and variation α . This value is near the calculated value according to Equation (5) and corresponds to the system state in which both solid phases do not alter their attitude of equilibrium, and this is possible only in the absence of the regulating effect of redox potential.

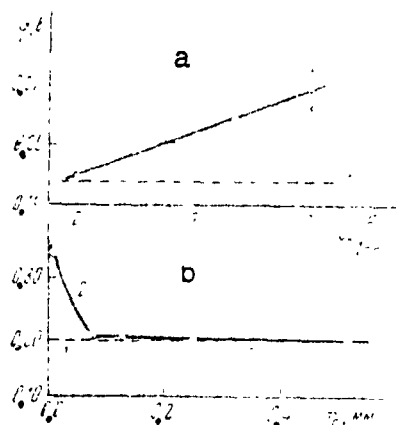


Figure 1. Standard potential of the mercury electrode dressed with EO-7 redoxite depending on:
a- degree of its oxidation and
b- granulation in a solution of 1 n. H_2SO_4 . Electrodes: 1-Hg and 2-Hg with resin.

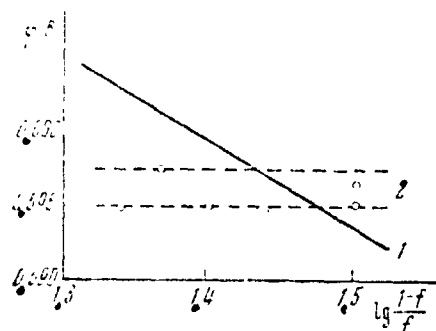


Figure 2. Standard potential of the platinum electrode depending on the degree of conversion of ferri-ions in 1n. solution H_2SO_4 with different dressing of EO-7 redoxite having a grain size of 0.25-0.50 mm:

1- theoretical line, 2- region of experimental value of the potentials.

According to the data of Figure 2, the standard potential of the platinum electrode acquires about the same value, and the fluctuations of this value are within limits of duplication of the experiments, independent of the amount of resin that has reacted with the solution of bivalent iron.

In differentiation to the quinone-hyquinone polymer redoxite, the solid metallic resins can be viewed, in an electrochemical regard, as being similar to porous electrodes, particularly with adequate electrical conductivity of the matrix. The potential is a function of the concentrations of the dissolved regions of the partial reaction. With a constant pH, the degree of conversion of the redoxite does not depend upon the value of its potential only if products of metal oxidation do not enter into the solution. From the kinetic curves (Figure 3) one can see that a dressing of the copper-containing EI-5 redoxite oxidized by aqueous oxygen has a fully determined effect on the value of the electrode potential, indicating electrochemical activity of the redoxite.

	Calc. accord. to (4)	Calc. accord. to (5)	Experiment		Calc. accord. to (4)	Calc. accord. to (5)	Experiment		Calc. accord. to (4)	Calc. accord. to (5)	Experiment
0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

* Translator's note: Commas in numbers represent decimal points.

After removing the dressing, the potential reverts to the initial state in all cases, excluding the acid solution, in which a certain amount of the ionogenic copper leaves the resin. Contact of the redoxite with neutral solutions leads to a change in the pH value as the result of migration of the ions of the sodium solution to ions of hydrogen of the sulfogroups. In buffer media, these changes are less noticeable and the potentials are distinguished by their high stability.

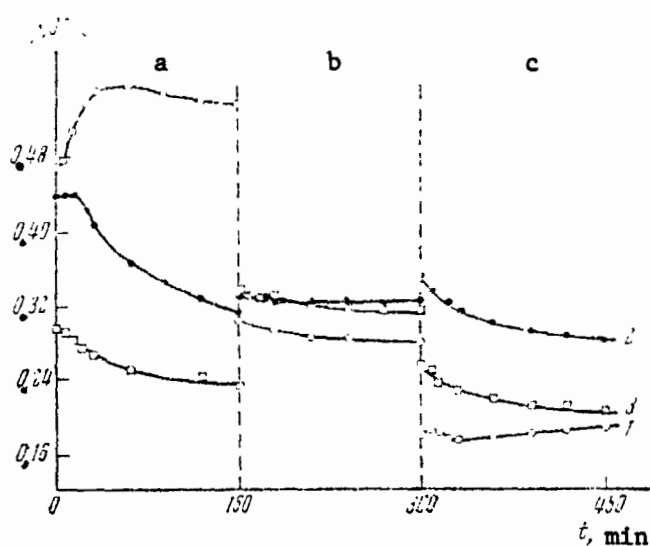


Figure 3. Kinetic curves of the potential of a mercury electrode dressed with the EI-5 oxidized redoxite in the following solutions: 1- 1.0n. H_2SO_4 ; 2-0.1n. Na_2SO_4 and 3-0.1n Na_2SO_4 +0.005m. Na_2CO_3 +0.005m. NaHCO_3 . Electrodes: a-Hg, b- Hg with resin dressing, c- Hg after the removal of the dressing.

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